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Field-scale study of the influence of differing remediation strategies on trace metal geochemistry in metal mine tailings from the Irish Midlands.

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ABSTRACT

Mine tailings represents a globally-significant source of potentially harmful elements (PHEs) to the environment. The management of large volumes of mine tailings represents a major challenge to the mining industry and environmental managers. This field-scale study evaluates the impact of two highly contrasting remediation approaches to the management and stabilisation of mine tailings. The geochemistry of the tailings, overlying amendment layers and vegetation are examined in the light of the different management approaches. Pseudo-total As, Cd, and Pb concentrations and solid-state partitioning (*speciation*), determined via sequential extraction, were established for two Tailings Management Facilities (TMFs) in Ireland subjected to: 1) a 'walk-away' approach (Silvermines) and 2) application of an amendment layer (Galmoy). PHE concentrations in roots and herbage of grasses growing on the TMFs were also determined. Results identify very different PHE concentration profiles with depth through the TMFs and the impact of remediation approach on concentrations and their potential bioavailability in the rooting zone of grass species. Data also highlight the importance of choice of grass species in remediation approaches and the benefits of relatively shallow-rooting *Agrostis capillaris* and *Festuca rubra* varieties. In addition, data from the Galmoy TMF indicate the importance of regional soil geochemistry for interpreting the influence of the PHE geochemistry of capping and amendment layers applied to mine tailings.

KEY WORDS: mine tailings, metals, phytoremediation, speciation, plant uptake

1. INTRODUCTION

The processing of metal ores produces significant quantities of fine-grained mine tailings, making the metal mining industry one of the largest waste producers in the world (Moncur et al., 2005). Mine tailings can contain highly elevated quantities of potentially harmful elements (PHEs), notably As, Cd and Pb (Bird et al., 2010; Nash and Fey, 2007). The storage of mine tailings has been a significant worldwide challenge for the mining industry for many years (CDC, 2007; Shu et al., 2001). Indeed, it is estimated that the production of solid mine waste, such as tailings, is in the region of several thousand million tonnes per year worldwide (Lottermoser, 2010). Challenges arise in relation to ensuring the physical and chemical stability of stored tailings (Hudson-Edwards et al., 2011), which have been described by Sima et al. (2011) as being one of the major sources of hazardous materials leading to the release of metals into the environment.

Metal contamination arising from the release of mine tailings into the environment has been demonstrated following: major tailings dam failures (e.g. Bird et al., 2008), aeolian transport of unconsolidated tailings (e.g. Grandlic et al., 2008) and the chemical leaching of metals (e.g. Palumbo-Roe et al., 2008). Surface and groundwater environments have been shown to be particularly vulnerable to contamination by the release of metals from deposits of mine tailings (Sharma and Al-Busaidi, 2001) as well as other mine drainage (Bearcock and Perkins, 2007; Perkins et al., 2006). In Europe, the environmental risk posed by mine tailings has been further highlighted by the development of the EU Mine Waste Directive (2006/21/EC), which has introduced new requirements for mine waste management in order to improve sustainability of practices, prevent accidents and reduce environment impact. This European legislation is not retrospective so that older, abandoned, mine sites are not subject to its control.

Inherent within effective management of mine tailings are attempts to ensure the physical and chemical stability of tailings and to minimize the release of metals into the local environment (Kim and Jung, 2011; Meggyes et al., 2008). Establishing networks to monitor metal release from tailings facilities is relatively straightforward, however, a much greater challenge is found in attempts to establish methods for effectively remediating mine tailings and minimizing long-term environmental impacts. Work by Pyatt et al. (2000) has demonstrated that metal release from unmanaged mine tailings can continue over 10s to 1000s of years. Remediation of mine tailings has commonly focused on ensuring physical and chemical stability; in the case of the latter, particularly on lowering oxidation rates in pyritic tailings. Revegetation has been identified as a potentially viable approach to tailings remediation (Tordoff et al., 2000). Approaches to this have ranged from direct hydro-seeding of tailings (Martínez-Ruiz et al., 2007), to capping with soil amendments (Palmer, 2006), geotextile membranes (Callery and Courtney, in press), rock backfill (Shu and Bradshaw, 1995).

Given their sedimentological, mineralogical and geochemical properties; mine tailings are very complex and highly reactive materials. Furthermore, they are often present within geochemically dynamic environments. Studies of approaches to tailings remediation have been carried out at a laboratory- and trial-scale (Lindsay et al., 2011; Mench et al., 2003; Mench et al., 2010; Moreno-Jimenez et al., 2011); however, relatively few have sought to evaluate the impact of remediation techniques on tailings geochemistry at the field-scale. The aims of this work are to investigate the longer-term impact of remediation practices on the geochemistry of mine tailings at two sites that have been subject to very different remediation strategies. The study focuses particularly upon the geochemistry of As, Cd and Pb given their noted environmental concern.

2. STUDY AREA

Sample collection focused upon two tailings management facilities (TMFs) in Ireland. The Pb/Zn mine at Galmoy in the Irish Midlands features a TMF under differing stages of remediation, ranging from active settling ponds to revegetated tailings (Figure 1). Mining at Galmoy primarily focused on the extraction of Zn and Pb ores in rock matrix

breccias at or towards the base of the Waulsortian Limestone (Lowther et al. 2003) (Balassone et al., 2008). The stratabound ore lenses are predominantly massive sulphides (Balassone et al., 2008), with ore grades ranging from c.10-13.5% (Zn) and c. 0.5-5.5% Pb during the operation of the mine. The sequence of mineralisation at Galmoy consists of a coarse-grained pyrite/marcasite assemblage followed by first, second and third generation sphalerite followed by late pyrite (Lowther et al., 2003). Galmoy's TMF became operational in 1997 and covers an area of c. 0.35 km^2. This study focused upon Phase 1 of the TMF, which has been filled to capacity with tailings and has been capped with a minimum 30 cm layer of diamicton and vegetated. The capping with diamicton was proscribed by local government with the material sourced from 'borrow pits' adjacent to the TMF. The site also contains thirteen 10 m^2 trial plots that were established in 2002 to evaluate the suitability of differing soil amendments and vegetation species (Table 1) as options for developing a long-term remediation solution.

The Gortmore TMF near Silvermines village (Figure 1) is an older facility than Galmoy, and was constructed in 1967 to store tailings from the processing of Zn and Pb ores at Garryard within the Silvermines mining district. Mining at Garryard produced 10.7 m tonnes of ore grading 7.4% Zn and 2.7% Pb, which produced 9 m tonnes of tailings; 7.7 m tonnes of which were stored in the Gortmore TMF (Stanley et al., 2010). The paragentic sequence at Silvermines has early heamatite/magnetite and barite followed by pyrite/marcasite before the development of sphalerite and galena together with Cu-Ag-As sulphides (Hitzman and Beaty, 2003). The TMF covers an area of 0.77 km^2 and contains a volume of ca. 5 m m^3 of material (Stanley et al., 2010). Following the cessation of mining activity in 1982, the TMF was effectively abandoned with little attention paid to remediation efforts. A dust-blow event in 1985 prompted attempts to vegetate the TMF surface through the simple addition of grass seed (Stanley et al., 2010), however, the vegetative cover is generally in poor condition, with evidence of ponding of rainwater. Release of metals from the site via drainage and wind-blown material have been the focus of environmental concerns (e.g. Aslibekion et al., 1999) and Pb concentrations in the upper 10 cm of the TMF have been previously reported as being in excess of 5000 mg kg^{-1} (McGrath et al., 2004). Mineralization at Silvermines is hosted predominantly within the basal Waulsortian Limestone and the underlying Ballysteen Limestone which lies on the basement rocks consisting of Silurian and Devonian Old Red Sandstone (Hitzman and Beaty, 2003). The geology of the area is dominated by the Silvermines Fault complex that was active during sedimentation and mineralization (Taylor and Andrew, 1978). The Zn and Pb sulphide ores are associated with non-sulphide deposits and are generally present in a stratabound morphology (Balassone et al., 2008).

3. SAMPLING AND ANALYTICAL METHODS

Sampling focused upon three broad locations: 1) the remediated phase of the Galmoy TMF, 2) the 13 trial plots established at Galmoy Mine, and 3) the Gortmore TMF near Silvermines. At Silvermines and the Galmoy trial plots push cores of a minimum 17 cm depth were collected through the overlying material and into the underlying tailings. At Silvermines, samples sites (n = 5) were spaced equidistantly along the centre of the TMF (Figure 1). On the Galmoy TMF (n = 4), given the depth of diamicton coverage, a pit was dug through this material to allow sampling through the overburden and the recovery of a core through the base of the pit into the underlying tailings. Samples of vegetation cover (roots and herbage) were collected from the Galmoy and SIlvermines TMFs at the site of each core. Herbage refers to the above-ground portion of the plant.

3.1. Analysis of particulate samples

All cores were cut into 2 cm sections and all samples were air-dried, disaggregated and sieved through a stainless steel mesh to isolate the <2mm fraction, which was retained for subsequent analysis. The pH of samples was determined by pH electrode (Hannah Instruments pH209) in a solution containing sample and deionized water in a 1:2.5 (w:v) ratio. Organic matter content was quantified in a sub-set of samples (providing on average 4 determinations per core) by the ignition of sample material at 375°C for 16 hours (Ball, 1964), the ash residue was

then further ignited at 850°C for 1 hour with any further loss taken as being representative of carbonate content (Avery and Bascomb, 1974). Whilst commonly being termed organic matter content, it must be noted that ignition of the sample may also case mass loss from sulphides, especially in samples of tailings. Samples were digested in concentrated aqua regia (HCl and HNO_3 in a 3:1 v/v ratio) with pseudo-total concentrations of As, Cd and Pb determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Accuracy (Table 2) and precision of analyses was monitored by the repeat analysis of the CANMET Till2 certified reference material (CRM). Precision was found to be 8.4% (As), 9.4% (Ca), 13.5% (Cd with concentrations < 0.5 mg kg^{-1}) and therefore generally below the 10% threshold commonly adopted by analysts (Hamilton, 1980).

A selection of samples (n = 155) were digested in 0.11 Moles L^{-1} acetic acid to provide an indication of As, Cd and Pb concentrations that could be considered as being potentially mobile and available for plant uptake (Bjerre and Schierup, 1985; Loring, 1981). Elemental concentrations were determined by ICP-MS. Analytical precision was monitored by the analysis of duplicate samples and found to be 9.5% (As and Pb) and 9.4% (Cd). Instrumental accuracy, determined by analysis of standard solutions was 1.6% (As), 3.1% (Cd) and 7.2% (Pb).

3.2. Analysis of herbage samples

The herbage samples were divided into root and above ground portions. Sediment was removed from the roots by repeated washing in milli-Q H_2O. All herbage samples were then subjected to sonication in a 0.05 % (v/v) solution of Triton X100 for 10 minutes before being rinsed three times with milli-Q H_2O. The samples were dried at <40°C before being milled to < 1 mm in an IKA MF 10.1 mill. Sub-samples of the milled herbage (0.25 g) were subjected to a rapid digestion procedure after Hustead (2004), where 5 mL of 50% (v/v) HNO_3 was added to the sample, in a 50 mL pyrex boiling tube, which was heated to 180-190°C for 10 minutes. The tubes were then cooled and 2.5 mL of concentrated HNO_3 was added before the tubes were covered and heated at 100°C for 1 hour. Finally the cooled solutions were filtered through Whatman number 1 filter papers and made up to 50 mL before being transferred to 30 mL LDPE bottles for storage.

3.3. Sequential extraction procedure

Finally, 28 samples were subjected to the BCR (Bureau of Community Reference) sequential extraction procedure (SEP) in order to evaluate the solid-state partitioning or *speciation* of PHEs (Quevauviller et al., 1993; Rauret et al., 1999). The four extractants used were: 1) 0.11 Moles L^{-1} acetic acid, 2) 0.5 Moles L^{-1} $NH_2OH.HCl$, 3) 8.8 Moles L^{-1} H_2O_2, and 4) concentrated *aqua regia*. This gave partitioning in four operationally-defined phases analogous to: 1) exchangeable, 2) Fe/Mn oxides, 3) organic matter/sulphides, and 4) residual metal forms. All supernatants were decanted into acid-washed plastic bottles and refrigerated prior to analysis. Between each phase of the SEP, samples were washed using 10 mL Milli-Q water. All reagents used were of Analar quality and reactions were performed in acid-washed 50 mL HDPE centrifuge tubes. Recovery of the SEP was determined by comparison of summed concentration in the four phases with values determined by a single *aqua regia* digest of blind duplicate samples (Bird et al., 2003; Li and Thornton, 2001). Recovery rates for the SEP ranged from 96 - 120 with a mean recovery of 111%. Precision of the SEP, determined by analysis of duplicate samples (n = 5) was found to be 9.9% (As), 9.3% (Cd) and 8.3% (Pb).

4. RESULTS AND DISCUSSION

4.1. pH, organic matter and carbonate content

The pH of material in the Silvermines TMF is generally lower than that at Galmoy (Table 3) with minimum (5.71), median (6.61) and maximum (7.38) pH values all lower than those at Galmoy (6.75, 7.39 and 8.37 respectively). This may be explained by lower carbonate content in material from the Silvermines TMF (4.8-18.7%) as well as the greater abundance (32.8%) of pyrite within the Silvermines tailings (Jordan and Mullen, 2006), compared to that in

ore at Galmoy (5-17%) (Hallewell et al., 2005). . Whilst the carbonate contents of material at the two locations are not statistically significantly different (Mann Whitney U Test; p = 0.1055), the Galmoy TMF and Galmoy trial plots contain higher mean and maximum carbonate content, which reflects the carbonate-dominated host geology (Balassone et al., 2008). Down profile trends in organic matter content are similar in all core samples from Galmoy, with highest organic matter content in the upper cores. At Galmoy maximum organic matter content ranges from 10 % to 18.5 % within the soil layers, reducing to less than 2 % in the underlying tailings material. The organic matter content of the Galmoy trial plots (Figure 2), which were constructed with 10-15 cm soil covering is generally higher than that of the Silvermines tailings pond (Figure 3) and certainly contains higher organic matter content at depth. For example, at 8-10 cm depth, mean organic matter content in the Galmoy trial plots is 6.4% compared to 0.7 % at Silvermines. The Galmoy TMF has organic matter content of 0.1-22% with greatest amounts in the upper 15 cm of the introduced capping material. On the basis of the mean % organic matter content, soils present on the Galmoy trial plots and Galmoy and Silvermines TMFs could be classed as mineralized, whereas peak % organic matter values in the upper profiles would be classified as humose (Ball, 1964). Lower organic matter content at Silvermines compared to Galmoy is likely to reflect both the differences in treatment and associated differences in vegetation development and creation of soil organic matter. The cores collected at Silvermines are characterised by an orange Fe-rich (average Fe content of 0.23%) layer (Munsell colour classification 5YR 6/5) of up to 15 cm thick that is located from approximately 5cm depth in the cores. This layer was clearly observable during sampling.

4.2. Pseudo-total PHE concentrations

In the Galmoy trial plots PHE concentrations range from 11-2440 mg kg^{-1} As, 0.7-39 mg kg^{-1} Cd and 31-2600 mg kg^{-1} Pb. The peak concentrations in the trial plots all occur in the lower profiles at 8-10 cm depth or below (Figure 4). Non paramtetric significant different analysis (Kruskall-Wallis H-Test) indicates that there is no significant difference in As or Pb concentrations between the thirteen different trial plots. Whilst higher concentrations in the underlying tailings are common to all plots, the analysis suggests that the type of amendment layer and vegetation cover has not resulted in statistically significant differences in As and Pb concentrations throughout the whole cores. The same analysis indicates that Cd concentrations are significantly lower ($p < 0.05$) in trial plots GT4 and GT10, although there is no significant difference in Cd concentrations amongst the remaining eleven plots. Unfortunately sample populations are too small to robustly analyse for significant differences between PHE concentrations in the amendment layers. However, non-parametric significant difference analysis (Mann-Whitney U Test), indicates that pseudo-total PHE concentration in the amendment layers are significantly lower ($p < 0.05$) than in the underlying tailings.

In samples collected from the Galmoy TMF concentrations range from 2-3200 mg kg^{-1} As, 0.25-122 mg kg^{-1} Cd and 11-21400 mg kg^{-1} Pb (Figure 5). The peak Pb concentration represents a single value of that magnitude, with the upper value in the remainder of samples being 9700 mg kg^{1}. As with the trial plots, maximum values occur at depth (below 50 cm) within the tailings material; characterized by higher carbonate content, indicative of the carbonate gangue material that constitutes much of the tailings material. The chemical data presented here demonstrate that the volume percentage of galena and sphalerite in the tailings material analysed range up to 2.3 and 4 % respectively with typical values being c.0.7 and c.2.2%, respectively. At Silvermines, mean (492 mg kg^{-1}) and peak (1040 mg kg^{-1-}) As concentrations are lower than those at Galmoy, however minimum, mean and peak, Cd and Pb concentrations are higher at Silvermines (Table 3). Data indicate that the Silvermine tailings contain volume percentages of galena and sphalerite with typical values c. 0.12% and c.1.5%, respectively. Non-parametric significant difference analysis (Mann-Whitney U Test) indicates that Cd ($p=0.0007$) and Pb ($p=0.0009$) concentrations in Silvermines and Galmoy samples are significantly different.

Arsenic and Pb concentrations in the Galmoy trial plots and TMF are strongly positively correlated carbonate content (Table 4). Reference to Figs. 3 and 4 show that in the trial plots this correlation has a clear vertical pattern which we

interpret to indicate the boundary between the amendment layer and the underlying tailings (at the time of sampling). The strength of correlation coefficients for the relationships between trace metal concentrations and pH, organic matter and carbonate content are notably lower for Silvermines than Galmoy. For samples for which loss on ignition data is available, there are statistically significant correlation relationships between organic matter content and Pb concentration ($r = 0.69$) and carbonate content and Cd concentration ($r = -0.70$).

The presence of elevated As concentrations, particularly within the tailings material, suggests the presence of arsenic-bearing minerals within the mined and processed material. Hitzman and Beaty (1996) state that iron sulphides are abundant in Silvermines and Galmoy with ores containing from 10 to 20% Fe and that most Irish zinc deposits contain minor arsenic-rich, antimony-poor tennantite as well as a number of Pb-As-Ag sulphosalt minerals. Elevated Pb concentrations, certainly within tailings material, are to be expected given the presence of Pb mineralization, whilst elevated Cd is believed to present in association with ZnS mineralization.

In the Galmoy trial plots and TMF, samples collected in the upper 10 cm and 50 cm, respectively comprise those collected within the layers of applied overburden. Within the trial plots, concentrations of As (20-2440 mg kg^{-1}), Cd (0.7-32 mg kg^{-1}) and Pb (11-1540 mg kg^{-1}) in the upper 10 cm are generally lower than those in material below. In the Galmoy TMF, concentrations of As (3-267 mg kg^{-1}) Cd (0.3-5.7 mg kg^{-1}) and Pb (19-985 mg kg^{-1}) are generally lower than in material from greater than 50 cm depth; certainly in the case of maximum concentrations. However, it is apparent that whilst concentrations in the coverings applied to the tailings material concentrations are lower than material below, particularly As concentrations in these upper layers often exceed critical concentrations for soils reported by Kabata-Pendias and Pendias (2001) (Table 5). Of the total number of samples collected between 0 and 10 cm or 0 and 50 cm depth in the trial pits and TMF respectively (n=80), only 23% of samples have As concentrations below 20 mg kg^{-1}. Exceedence of critical Cd (30% of samples) and Pb (52% of samples) concentrations is lower, but still present. Concentrations of As, Cd and Pb in the applied soil layers at Galmoy also exceed the national average concentrations for Irish soils (Table 5) by up to 24 (As), 8 (Cd) and 10 (Pb) times with respect to average concentrations.

Cadmium and Pb concentrations at Silvermines are higher than at Galmoy and mean PHE concentrations at Silvermines are 54 (As), 52 (Cd) and 73 (Pb) times higher than average concentrations determined in Irish soils. All samples from the Silvermines TMF contain As, Cd and Pb at concentrations above the critical range for soils (Table 5). Unlike at Galmoy, in cores recovered from the Silvermines TMF, peak concentrations occur in the upper 5 cm (Figure 6). These peak concentrations constitute enrichment factors of 115 (As), 256 (Cd) and 561 (Pb) times above Irish average concentrations. Whilst the Silvermines TMF has not been subject to extensive capping with overburden, one may expect highest metal concentrations to be associated with tailings material at depth. However, the presence of peak metal and As concentrations in the upper 5 cm of the Silvermines TMF indicates that there has been the enrichment of metal levels within material in the upper core. Importantly, these highly elevated concentrations will be in the rooting zones for vegetation cover and may help to explain the generally poor nature of vegetation cover on the Silvermines TMF (Environmental Protection Agency, 2004). The exact cause of enrichment in the upper profile is unknown, however, it possible that the Fe-rich layer identified previously may be acting as a focus for PHE-enrichment, perhaps from pore-water.

4.3. Acetic Acid-soluble PHE concentrations and speciation

Within the Galmoy trial plots acetic acid-soluble PHE concentrations are in the range <0.1-3.4 mg kg^{-1} (As), 0.1-16 mg kg^{-1} (Cd) and 0.2-1340 mg kg^{-1} (Pb). These concentrations are broadly similar in the Galmoy TMF (Table 3), however the maximum Pb concentration in the TMF is somewhat higher at 6800 mg kg^{-1}. As seen with pseudo-total concentrations, acetic acid-soluble As is lower in the Silvermines TMF (<0.1-1.9 mg kg^{-1}), whilst Cd (1.2-33 mg kg^{-1}) and Pb (30-4100 mg kg^{-1}) concentrations are similar to, or moderately higher, at Silvermines. Calculating the acetic-acid soluble concentration, i.e. that which could be termed potentially bioavailable (Loring, 1981), as a percentage of

the pseudo total concentration (Table 3) indicates that on average acetic acid-soluble As concentrations are less than 2% of the pseudo-total concentrations. Importantly, coupled with the relatively low acetic-acid-soluble As concentrations, this would suggest that As will be largely unavailable for plant uptake. This is further supported by speciation data that indicated As is predominantly present in the residual phase at all sites (Figure 7). Highest percentage partitioning of As in the residual phase generally occurs in material with the highest total As concentrations, which in the case of the Galmoy trial plots and TMF is the tailings material at depth and at Silvermines material in the upper 10 cm. Exceptions to the dominance of the residual phase occur in the upper parts of the Galmoy trial plots and TMF (Figure 7). Overall, it is apparent that As is strongly bound within mineral structures, will be relatively immobile and be of lower environmental significance (c.f. Bird et al., 2003) than the pseudo-total concentrations alone may suggest. It should be noted however, that acid generation in tailings may increase the potential for the dissolution of some tightly-bound PHEs. For example, tailings at Silvermines have been reported as having an acid producing potential of 221-474 kg $CaCO_3$/tonne of tailings (Golder Associates, unpublished).

On average acetic acetic-soluble Cd concentrations are 28% (Galmoy trial plots), 22% (Silvermines TMF) and 9% (Galmoy TMF) of pseudo-total concentrations. Cadmium is known to be a generally mobile element (Beesley et al., 2010) and therefore its greater presence in the more loosely-bound exchangeable phase (Figure 8) is unsurprising. Importantly, the depth of maximum acetic acid-soluble concentrations in each core is on average 16 cm in the Galmoy trial plots, 10 cm on the Silvermines TMF and at >1 m depth on the Galmoy TMF. Certainly in the case of Galmoy, this would mean that material containing the highest weakly-bound Cd occurs in the lower part of the profiles. In the upper profiles at Galmoy, Cd is mostly associated with the Fe/Mn oxides and organic matter/sulphide phases. At Silvermines, whilst the maximum Cd partitioning occurs at 0-2 cm depth in core SC4 (90% associated with the Fe/Mn oxide phase), mean Cd partitioning at Silvermines is greatest with the organic matter/sulphide phase (Figure 8). The low organic matter content in sub-surface samples (0.8%) at Silvermines, may indicate that this partitioning is associated particularly with sulphides (Bird et al., 2008).

Lead is generally predominantly associated with the Fe/Mn oxide phase in the surface samples (< 10 cm) at both Galmoy and Silvermines (Figure 9) and mirrors findings of other studies into the speciation of Pb (e.g. Gomez-Alvarez et al., 2011; Reis et al., 2012). The importance of Fe/Mn oxides in the partitioning of Pb is particularly dominant in higher pH environments (Terzano et al., 2007) such as those found at Galmoy (pH range of 7.02-8.1). With increasing depth the importance of the Fe/Mn oxide phase reduces, with greater proportions of Pb present in the 'exchangeable' at all sites (Figure 9), mirroring in the case of Galmoy, an increase in PHE concentrations. The role of the organic matter/sulphide phase and residual phases also increases at depth at Galmoy, with the former phase likely to be residues of Pb sulphide minerals present within tailings material. On average acetic acid-soluble Pb concentrations peak at 20 cm depth in the Galmoy trial plots and >1 m depth on the Galmoy TMF. For Silvermines, peak acetic acid-soluble Pb concentrations occur on average at 8 cm depth with these concentrations representing 0.4-94% of the pseudo total concentration.

4.4. Potential uptake to plants and implications for TMF remediation

In samples of roots and herbage from the Galmoy and Silvermines TMFs, PHE concentrations are lower in the herbage than in roots (Figure 10). At Silvermines PHE concentrations in herbage are 0.6 – 57 times greater in the roots, whilst at Galmoy the enrichment in the roots compared to the herbage is lower (0.5 - 11). The much higher PHE concentrations in the root matter on the Silvermines TMF (e.g. up to 670 mg kg^{-1} Pb), is very likely to reflect the location of peak Pb concentrations in the growing media, which occur within the upper 5 cm. In contrast, maximum PHE concentrations in root material growing on the Galmoy TMF, subject to a ≥30 cm amendment layer and with maximum PHE concentrations at >50 cm depth, are 7 – 13 times lower than those at Silvermines (Figure 10). Calculation of a bioconcentration factor (BCF) (equation 1) suggests no accumulation of PHEs in the roots of grass growing on the Galmoy and Silvermines TMF (Table 6), as BCFs are <1 (Serbula et al., 2014), indeed, whilst root PHE

concentrations are higher at Silvermines, maximum BCFs are lower than for Galmoy, given the very high PHE concentrations in the growing medium. The data suggest that grass species growing on the Silvermines and Galmoy TMFs are relatively successful in excluding PHEs, taken up by the roots, from transferring to the remainder of the plant. Translocation factors (TF; equation 2) are <1 at Silvermines suggesting that there has not been transfer of PHEs from roots to herbage. At Galmoy all TFs <1, with the exception of one site each for Cd (TF = 1.19) and Pb (TF = 2.12), which suggests that there has been some limited uptake of Cd and Pb to herbage. With the exception of Pb in herbage at Silvermines, maximum PHE concentrations in herbage on the Galmoy and Silvermines TMFs are within the normal ranges for plants (Table 5) and all maximum PHE concentrations are below the upper threshold of the concentration ranges that could be considered excessive in leaf tissue (Table 5). Low TFs bode well for potential future use of remediated TMFs for uses including pastoral agriculture even at Silvermines where the soil layer is very thin.

$$BCF = C_{root}/C_{soil} \qquad \text{Equation 1}$$

Where C_{root} is the PHE concentration in the roots and C_{soil} is the PHE concentration in soil.

$$TF = C_{shoot}/C_{root} \qquad \text{Equation 2}$$

Where C_{shoot} is the PHE concentration in the shoots and C_{root} is the PHE concentration in roots.

Whilst there is no As and Cd herbage data for the Galmoy trial plots, analysis of Pb concentrations in herbage from the Galmoy trial plots (Galmoy Mines Ltd, unpublished) indicates that these are highest in herbage collected in the spring-time (Figure 11). Average Pb concentrations in the herbage of the different plots ranged from 7.4 mg kg^{-1} to 27.1 mg kg^{-1}, with the highest average (and maximum concentration: 94 mg kg^{-1}) occurring in plot 7, which had a 15 cm coverage of topsoil but no addition of compost. The lowest average concentration is found in herbage from plot 4, which also has the lowest variability in concentrations between sample periods (standard deviation of 3.1). Plot 4 has thicker (15 cm) addition of topsoil and compost and was sown with the *Festuca rubra Pernille* grass variety. This variety was also sown in plots 6A and 6B (along with *Poa compressa Reubens*) but with thinner top soil additions of 8 cm and 13 cm, respectively. However, mean Pb concentrations in plots 6A and 6B are still lower than those in eight other trial plots that were given thicker amendment layers, but sown with different grass varieties. Lead concentrations were found to be generally highest in April, previous studies of Pb uptake to grasses grown on contaminated soils and tailings have found concentrations to be highest in winter months (e.g. Crilly et al., 1998; Smith et al., 2009), which may influence the suitability of such land for use in grazing at certain times of the year. What is also apparent is that ingestion of PHEs by animals grazing on such grass may occur from soils adhering to the grass as much as from PHEs within the plant.

The lower concentrations in the Galmoy TMF herbage, and in the trial plots compared to herbage grown on metal rich soils reported by other studies, are indicative of the importance of soil cover thickness and plant species in influencing the potential for plant uptake. The thicker amendment layer of the TMF, with its lower Pb concentrations, provides a more effective barrier against plant uptake of Pb (and other PHEs) in underlying tailings. Data collated by Canadell et al. (1996) for over 90 species of temperate grass growing on various soil types demonstrates a maximum rooting depth of 1.2-6.3 m, which would potentially give rise to root penetration into underlying tailings material. However, *Agrostis capillaris* and *Festuca rubra*, which were the species planted at Galmoy are species that have predominantly shallow root systems. Bolinder et al. (2002) reported that *Agrostis capillaris* has 80% of its root volume within the upper 15cm of the soil profile, whilst Brown et al. (2010) demonstrated that the root volume of *Festuca rubra* in the upper 7.6 cm of the soil profile ranged from 61-66%. Data presented by Courtney (2013) for Pb concentrations in *Agrostis capillaris* and *Festuca rubra* growing on bare tailings were on average 1243 mg kg^{-1}, much higher than at Galmoy and demonstrating the benefits of an

amendment layer. The data from Galmoy indicate that a 15 cm amendment layer may not be sufficient to prevent Pb uptake into herbage exceeding normal levels and that a thicker, although more expensive, amendment layer is preferable. What is apparent, is that whilst mean PHE concentrations in herbage from the Galmoy TMF are within the normal range for leaf tissue, despite a ≥30 cm amendment layer, detectable PHE concentrations are present. Data have shown that the amendment layer on the Galmoy TMF does contain As concentrations above critical soil concentration (Table 5). Whilst it is possible that the As, and other PHEs, are sourced from the underlying tailings, it is also possible that the PHEs represent natural geogenic loading to the material in its source area. It is unknown exactly where the diamicton used for the amendment layer was sourced from, however, the Galmoy mine lies on the north-west edge of an area of higher soil As concentrations; as identified in the Soil Geochemical Atlas of Ireland (Fay et al., 2007). Soil As concentration in the Galmoy area (9.1-12 mg kg^{-1}), generally lie within the 75th percentile of nationally-monitored concentrations, with soil As levels increasing to >15 mg kg^{-1} within c. 50 km. Whilst, further work is required firmly to establish the source of As in amendment layers; the data highlight the importance of awareness of the geochemistry of amendments layers during remediation projects, as well as the geochemistry of waste material.

5. CONCLUSIONS

Determination of PHE concentrations from two differently-managed and remediated TMFs, has identified clear resultant differences in the geochemistry of TMF materials and vegetation growing upon them. A walk-away approach results in a PHE-rich environment, notably within the upper portions of the tailings material and resulted in high PHE concentrations particularly in the roots of grasses growing on the TMF, despite relatively low % occurrence of more loosely-bound species. Application of an amendment layer has been shown to create a rooting zone with much lower PHE concentrations and result in grasses growing in that material having PHE burdens of up to 13 times less. Data from this study suggest that remediation strategies should carefully consider the depth and geochemistry of applied amendment layers, particularly in relation to the rooting characteristics of vegetation intended for planting; and that shallow-rooting (grass) species offer distinct advantages in reducing metal uptake from material below amendment layers. In addition, Pb concentrations in grass varieties grown upon amended tailings have demonstrated a tendency for higher concentrations during spring months; this may be of relevance where revegetated tailings is intended for future use for animal grazing.

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Table 1. Grass types and organic substrates used in trial plots at Galmoy mine.

Plot	Substrate	Grass variety	Plot	Substrate	Grass variety
1	Bare tailings	Bardot, Barclay, Providence, Merlin	7	Topsoil (15 cm)	Bardot, Barclay, Providence, Merlin
2	Topsoil & compost (10cm)	Barclay	8	Topsoil & compost (13 cm)	Highland
3	Topsoil & compost (13 cm)	Barcrown	9	Topsoil & compost (15 cm)	Bardot
4	Topsoil & compost (15 cm)	Pernille	10	Topsoil & compost (15 cm)	Providence
5	Topsoil & compost (13 cm)	Merlin	11	Topsoil & compost (15 cm)	Heriot
6a	Topsoil & compost (13 cm)	Pernille & Reubens	12	Topsoil & compost (15 cm)	Reubens
6b	Topsoil (8 cm)	Pernille & Reubens			

Bardot: Colonial Bentgrass (*Agrostis capillaris*)
Barclay: Perennial Ryegrass (*Lolium perenne*)
Providence: Bentgrass (*Agrostis capillaris*)
Merlin: Bentgrass (*Agrostis capillaris 'merlin'*)
Barcrown: Red Fescue (*Festuca rubra*)
Pernille: Red Fescue (*Festuca rubra*)
Reubens: Canada Bluegrass (*Poa compressa*)
Highland: Highland Bentgrass (*Agrostis capillaris*)
Heriot: Browntip Bentgrass (*Agrostis capillaris*)

Table 2. Analytical Quality Control of aqua regia digest versus CANMET Till2 CRM.

	As	Cd	Pb
Aqua Regia digests of CANMET Till2 CRM			
Certified (mg kg^{-1})	22	0.3	21
Measured (mg kg^{-1})	17±1.4	0.37±0.04	26±2.3

Table 3. Mean* and range of soil properties and PHE concentrations in samples from Galmoy and Silvermines.

	Galmoy trial plots	**Galmoy TMF**	**Silvermines TMF**
Soil properties			
n	66	26	30
pH	7.47 (7.02 – 8.1)	7.39 (6.75 – 8.37)	6.61 (5.71 – 7.38)
Organic matter (%)	6.6 (0.2 - 18.5)	5.1 (0.1 – 22)	3.36 (0.1 – 29.6)
Carbonates (%)	15.6 (4.2 – 32)	16 (6.1 - 36)	11.3 (4.8 – 18.7)
Pseudo-total PHE content			
n	127	46	56
As (mg kg^{-1})	820 (11 – 2450)	1040 (2 – 3230)	500 (190 – 1040)
Cd (mg kg^{-1})	11 (0.7 – 40)	22 (0.2 – 120)	31 (13 – 150)
Pb (mg kg^{-1})	930 (31 – 2600)	2760 (12 – 21500)	2280 (620 – 125200)
Acetic acid-soluble PHE content			
n	67	30	30
As (mg kg^{-1})	0.8 (0.1 – 3.4)	0.9 (<0.1 – 4.5)	0.2 (<0.1 – 1.9)
Cd (mg kg^{-1})	3.8 (0.1 – 17)	4.2 (<0.1 – 10)	7 (1.2 – 33)
Pb (mg kg^{-1})	99 (<0.1 – 1340)	2013 (5 – 6800)	1320 (30 – 4120)

*median in the case of pH

Table 4. Correlation coefficients for the relationship between pH, organic matter (OM) and carbonate content with PHE concentrations

	Galmoy trial plots			Galmoy TMF			Silvermines TMF		
	As	Cd	Pb	As	Cd	Pb	As	Cd	Pb
pH	-0.48**	-0.56**	-0.51**	-0.57**	-0.62**	-0.62**	-0.32	-0.14	0.12
OM	-0.82**	-0.75**	-0.77**	-0.35	-0.32	-0.26	0.3	0.33	0.71**
Carbonate	0.78**	0.79**	0.70**	-0.51**	-0.58**	-0.56**	-0.47**	-0.72**	-0.29

*Significant at 95% confidence level.

**Significant at 99% confidence level.

Table 5. Summary of mean (with range in brackets) PHE concentrations in Irish soils and threshold PHE concentrations in soils and plants (concentrations in mg kg^{-1} except for pH).

Sample	**As**	**Cd**	**Pb**	**pH**
Irish soils[a, b]	9.04 / *7.25* (0.2-122.7)	0.56 / *0.33* (0.02-15)	31 / *24.8* (1.1-2634)	5.33 / *5.3* (3.2-7.7)
Critical soil concentration[c]	20-50	3-8	100-400	--
Excessive concentrations in leaf tissue[d]	5-20	3-30	30-300	--
Normal range in plants[c]	0.02-7	0.1-2.4	0.2-20	--

[a]Environmental Protection Agency. Samples digested in a mixture of HF, $HClO_4$, HCl and HNO_3 acids with analysis by ICP-MS (n = 1310).

[b]50^{th} percentile value given in italics

[c]Kabata-Pendias and Pendias (2001)

[d]Bowen (1979)

Table 6. Range of biocentration factors (BCF) and, translocation factors (TF) for grass growing on the Galmoy and Silvermines TMFs.

	BCF	**TF**
	Galmoy TMF	
As	0.13-0.34	0.08-0.24
Cd	0.18-0.25	0.36-1.19
Pb	0.07-0.23	0.19-2.12
	Silvermines TMF	
As	<0.01-0.06	0.02-0.63
Cd	0.08-0.16	0.07-0.18
Pb	<0.01-0.25	0.04-0.59

Figure captions

Figure 1. Schematic and location of the Galmoy and Silvermines TMFs and the location of TMF sample sites.

Figure 2. Down-core pH, organic matter and carbonate content in samples from the Galmoy trial plots.

Figure 3. Down-core pH, organic matter and carbonate content in samples from the Silvermines TMF.

Figure 4. Down-core PHE concentrations in the samples collected from the Galmoy trial plots.

Figure 5. Down-core PHE concentrations in the samples collected from the Galmoy TMF.

Figure 6. Down-core PHE concentrations in samples collected from the Silvermines TMF.

Figure 7. Down-core speciation of As in samples collected from the Galmoy and Silvermines TMFs and Galmoy trial plots.

Figure 8. Down-core speciation of Cd in samples collected from the Galmoy and Silvermines TMFs and Galmoy trial plots.

Figure 9. Down-core speciation of Pb in samples collected from the Galmoy and Silvermines TMFs and Galmoy trial plots.

Figure 10. Minimum, mean and maximum PHE concentrations in root and herbage material sampled from the Silvermines (n = 5) and Galmoy (n = 4) TMFs.

Figure 11. Pb concentrations in herbage sampled from the Galmoy trial plots. Pb concentrations were determined following an aqua regia digest; data from Galmoy Mines Limited (unpublished). Grey shading represents the 0.2-20 mg kg^{-1} normal range for Pb in plants Kabata-Pendias and Pendias (2001).

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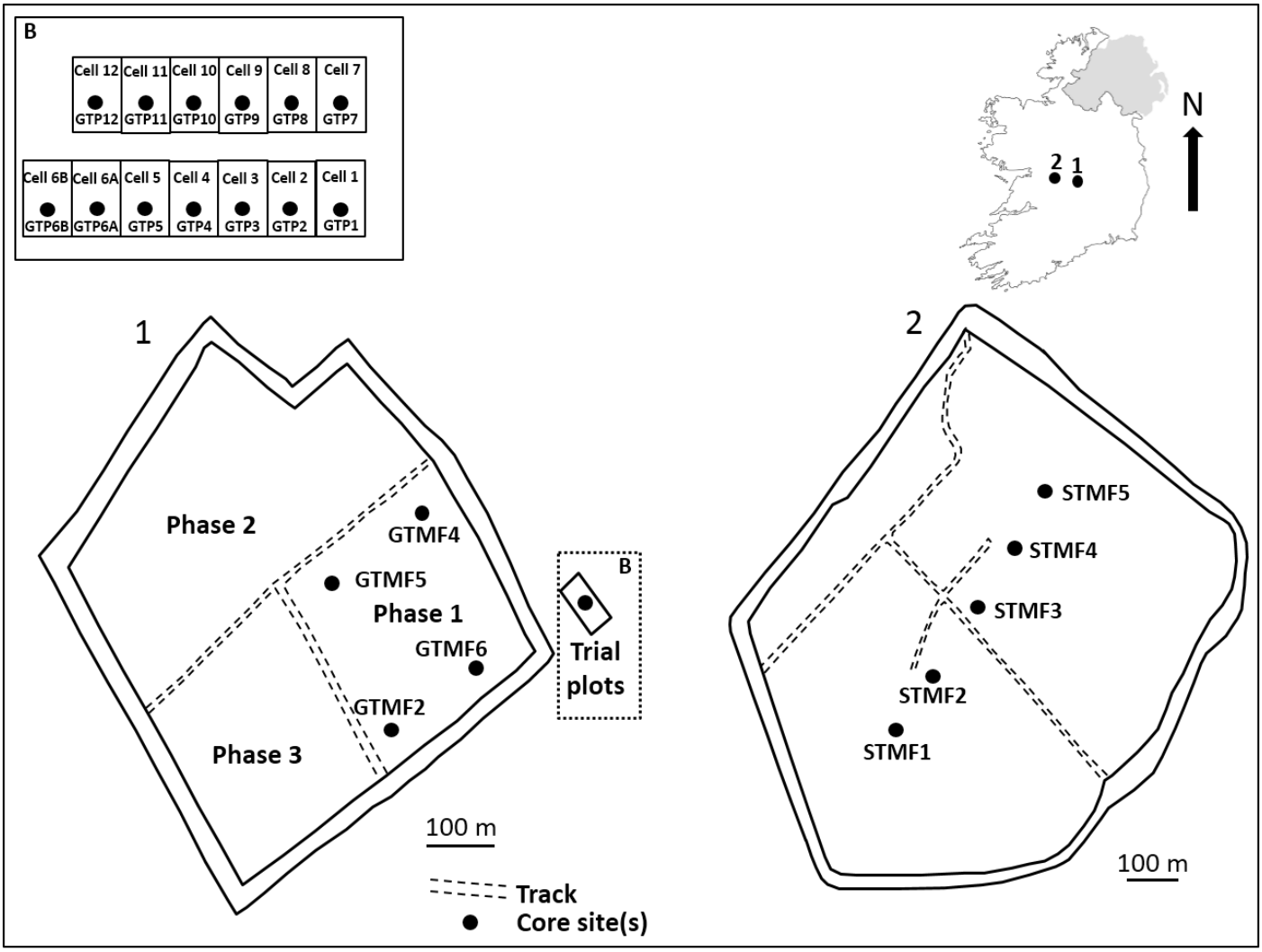
B
Cell 12
GTP12
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Cell 10
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Cell 9
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Cell 8
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Cell 6A
GTP6A
Cell 5
GTP5
Cell 4
GTP4
Cell 3
GTP3
Cell 2
GTP2
Cell 1
GTP1
N
2
1
1
Phase 2
GTMF4
GTMF5
Phase 1
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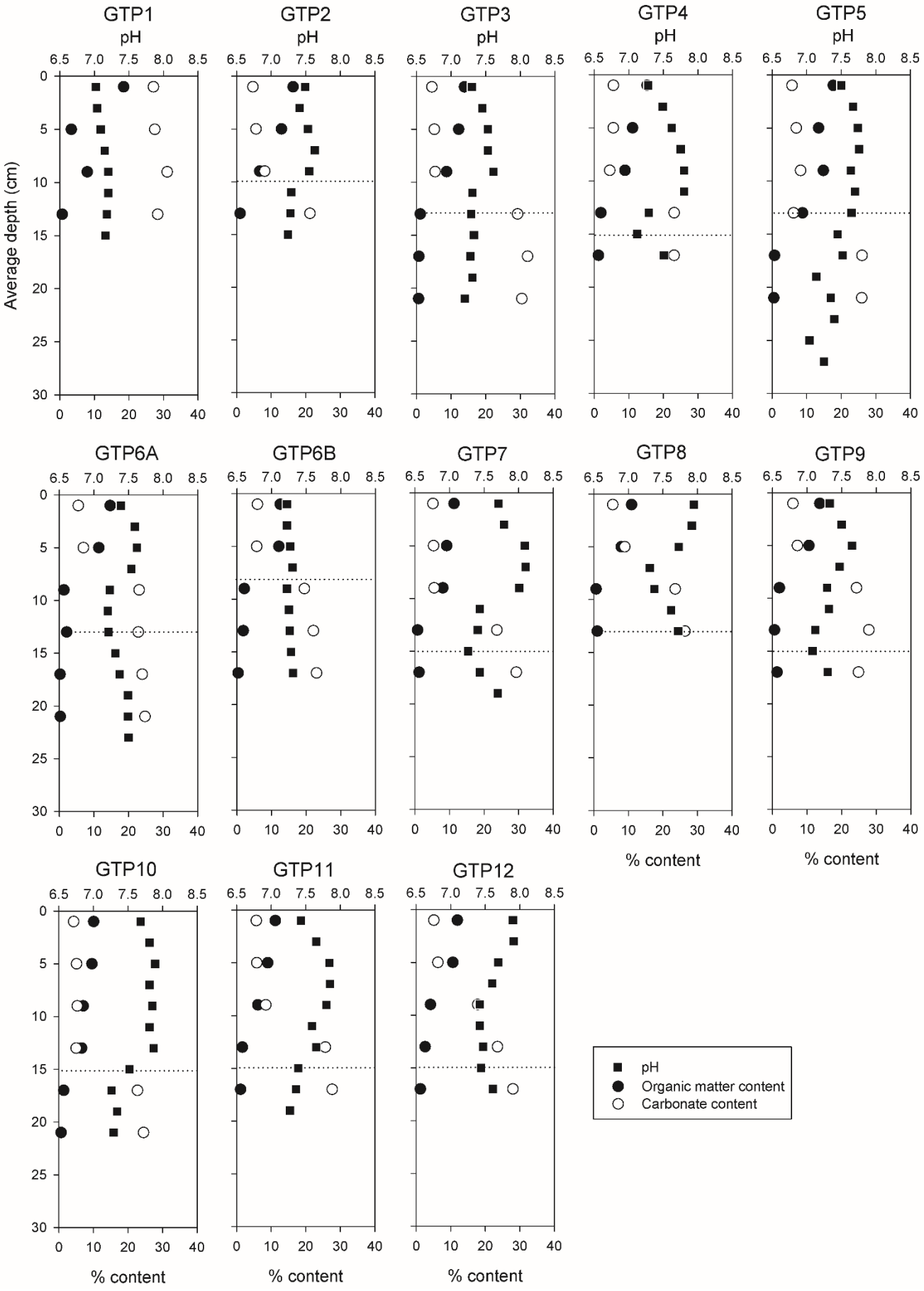
B
Trial plots
100 m
Track
Core site(s)
2
STMF5
STMF4
STMF3
STMF2
STMF1
100 m

Figure 1


GTP1
GTP2
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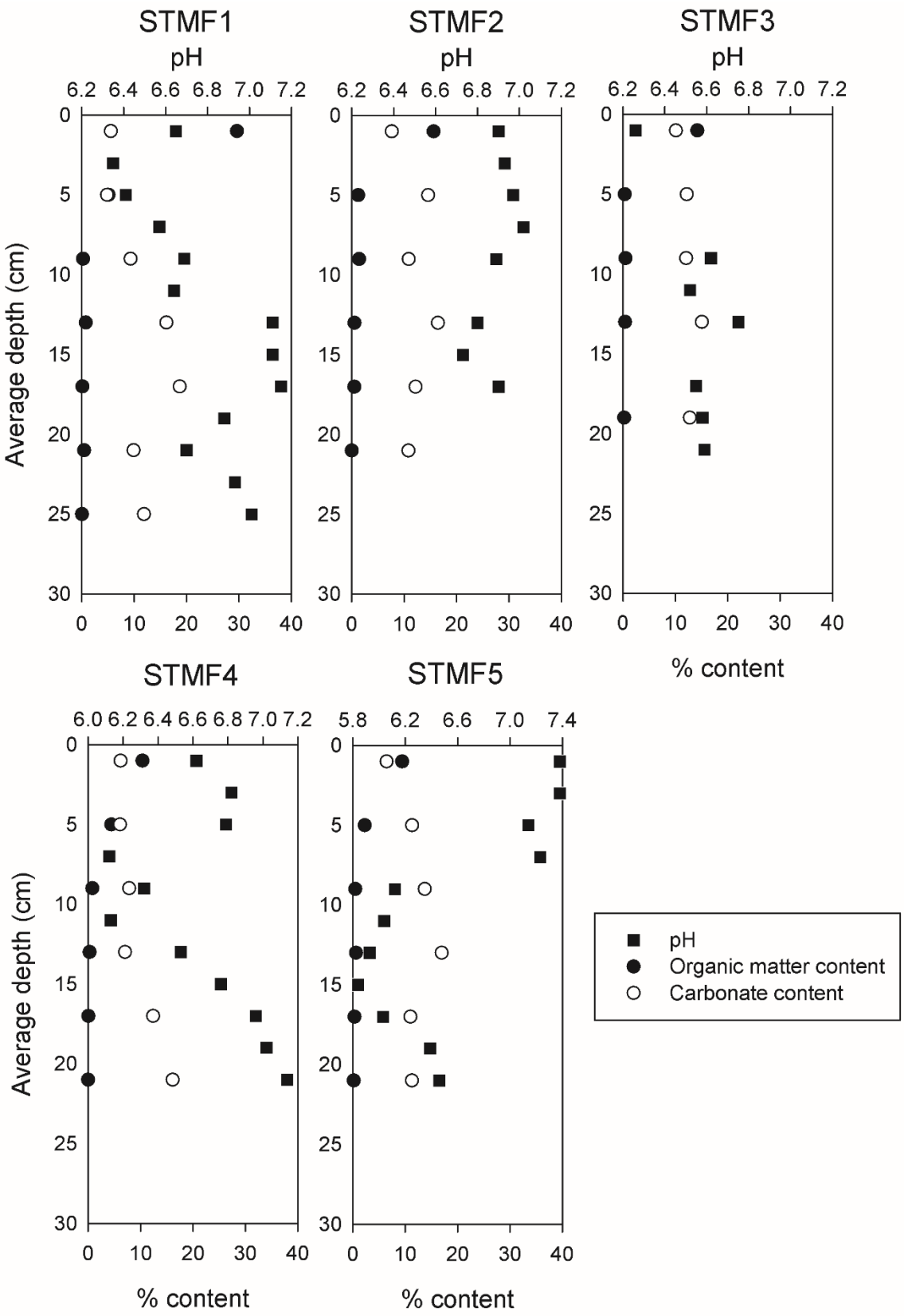
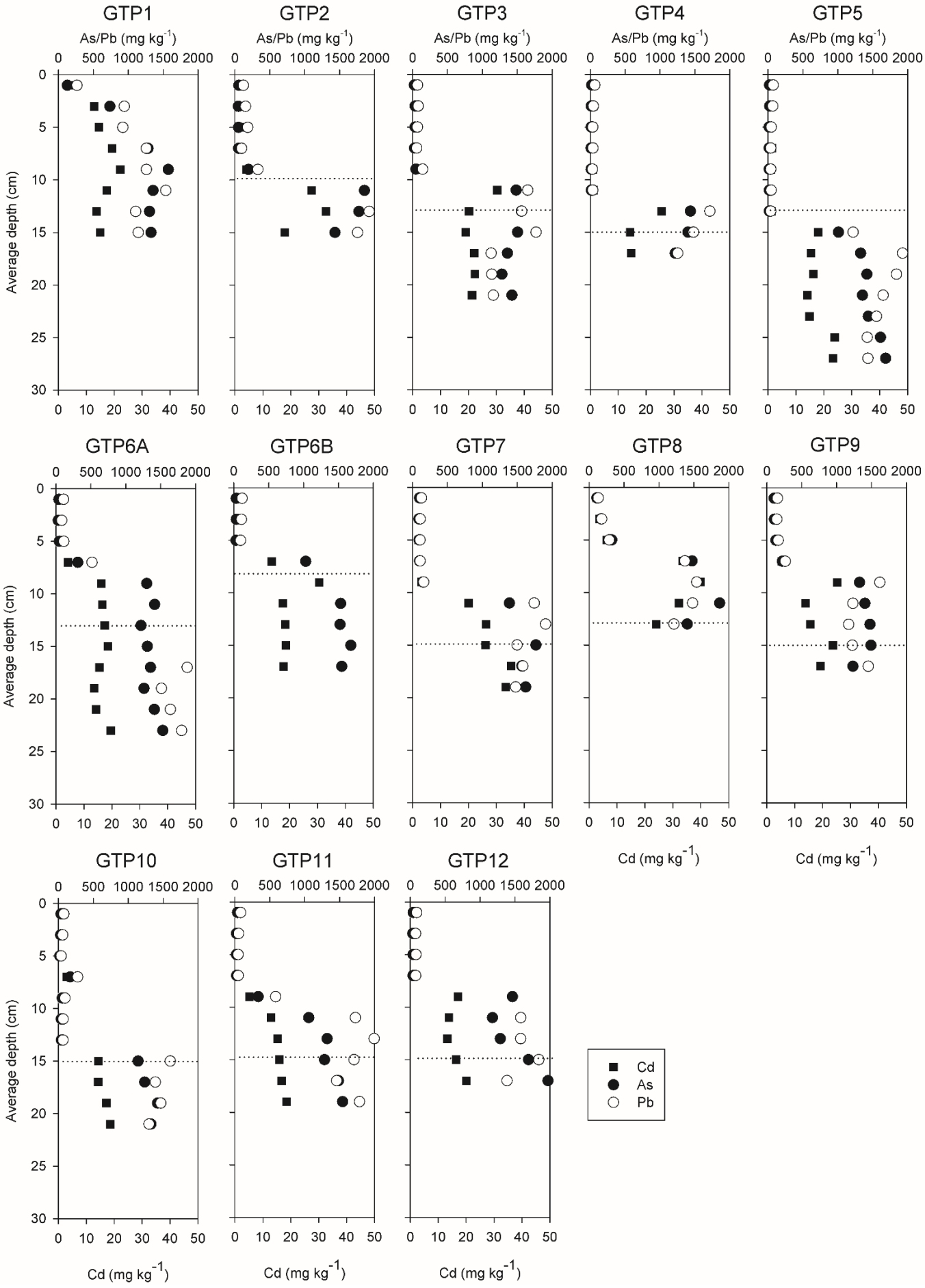
GTP9
GTP10
GTP11
GTP12
pH
Average depth (cm)
% content
pH
Organic matter content
Carbonate content

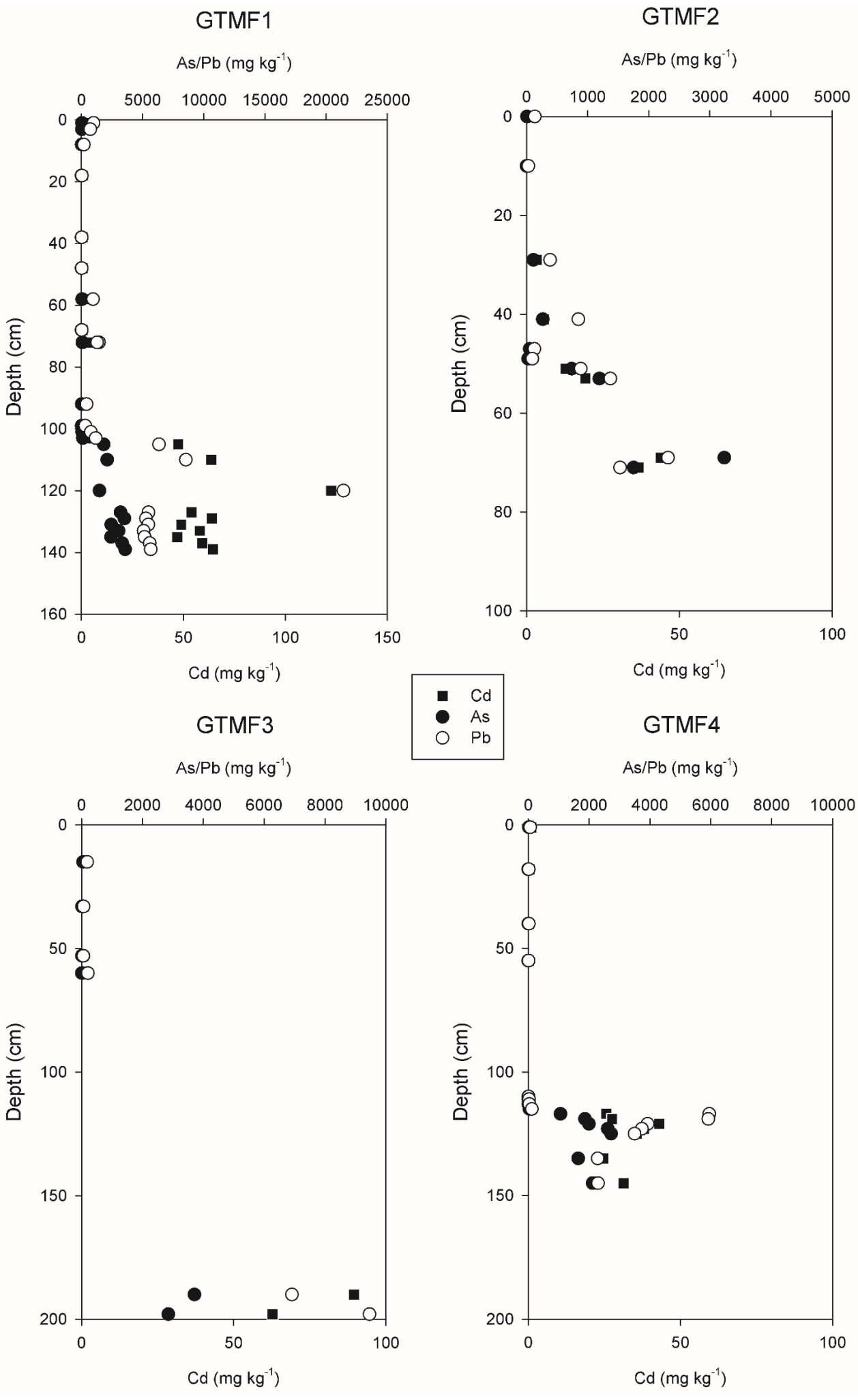
735
736


STMF1
STMF2
STMF3
STMF4
STMF5
pH
Average depth (cm)
% content
pH
Organic matter content
Carbonate content

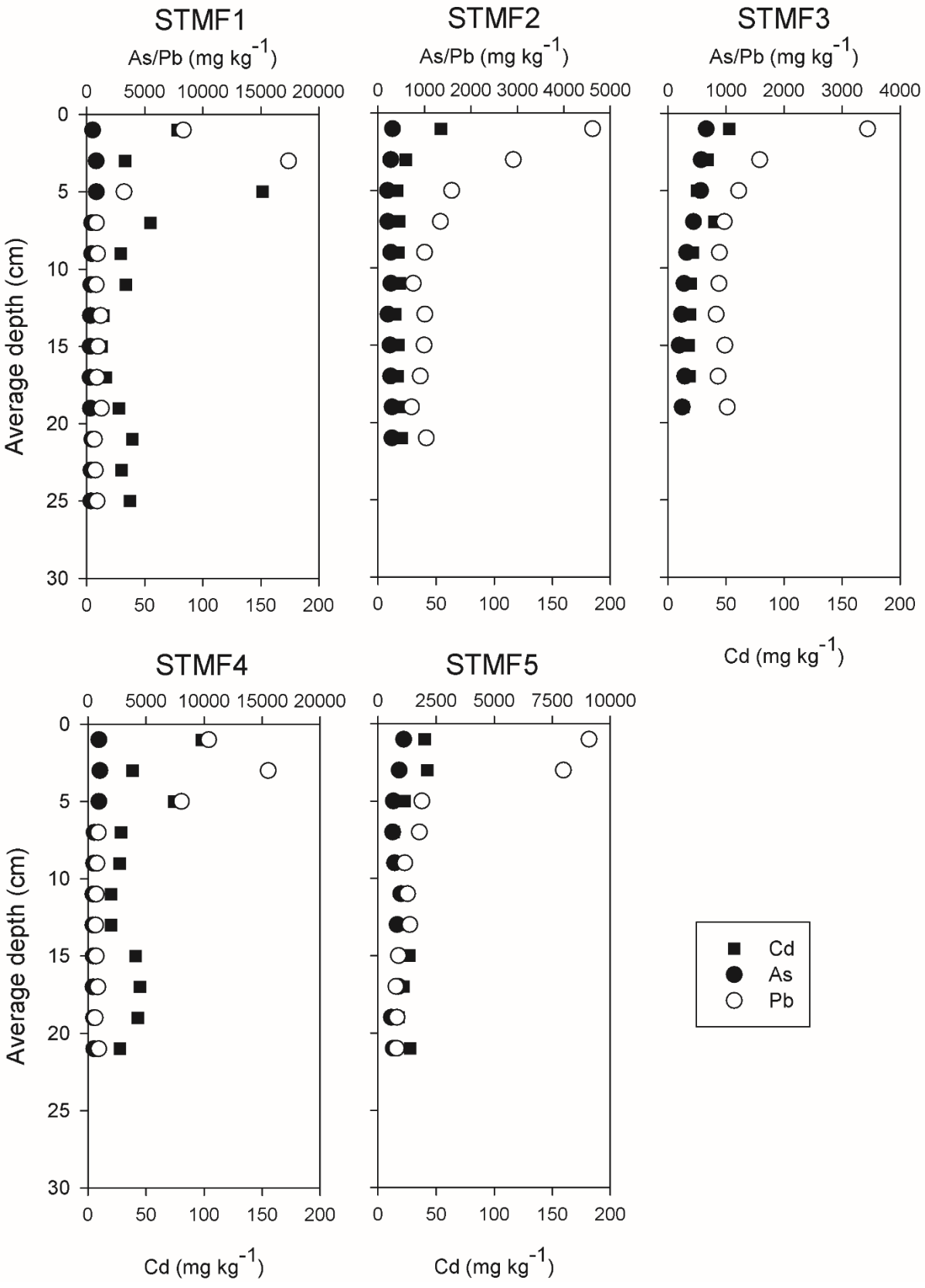
737


GTP1
GTP2
GTP3
GTP4
GTP5
GTP6A
GTP6B
GTP7
GTP8
GTP9
GTP10
GTP11
GTP12
As/Pb (mg kg-1)
Cd (mg kg-1)
Average depth (cm)
Cd
As
Pb

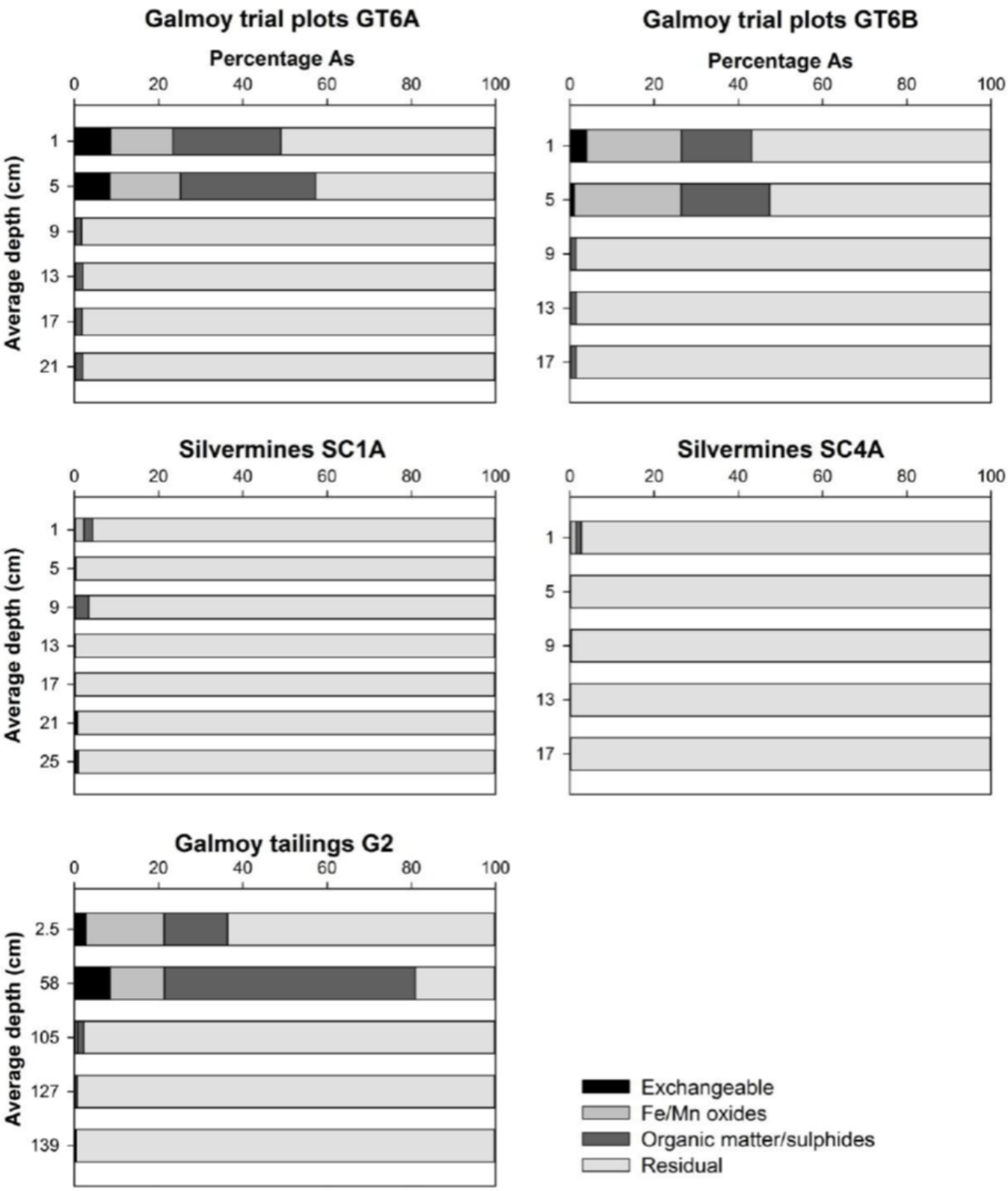
738


GTMF1
As/Pb (mg kg-1)
0
5000
10000
15000
20000
25000
Depth (cm)
0
20
40
60
80
100
120
140
160
0
50
100
150
Cd (mg kg-1)
GTMF2
As/Pb (mg kg-1)
0
1000
2000
3000
4000
5000
Depth (cm)
0
20
40
60
80
100
0
50
100
Cd (mg kg-1)
Cd
As
Pb
GTMF3
As/Pb (mg kg-1)
0
2000
4000
6000
8000
10000
Depth (cm)
0
50
100
150
200
0
50
100
Cd (mg kg-1)
GTMF4
As/Pb (mg kg-1)
0
2000
4000
6000
8000
10000
Depth (cm)
0
50
100
150
200
0
50
100
Cd (mg kg-1)

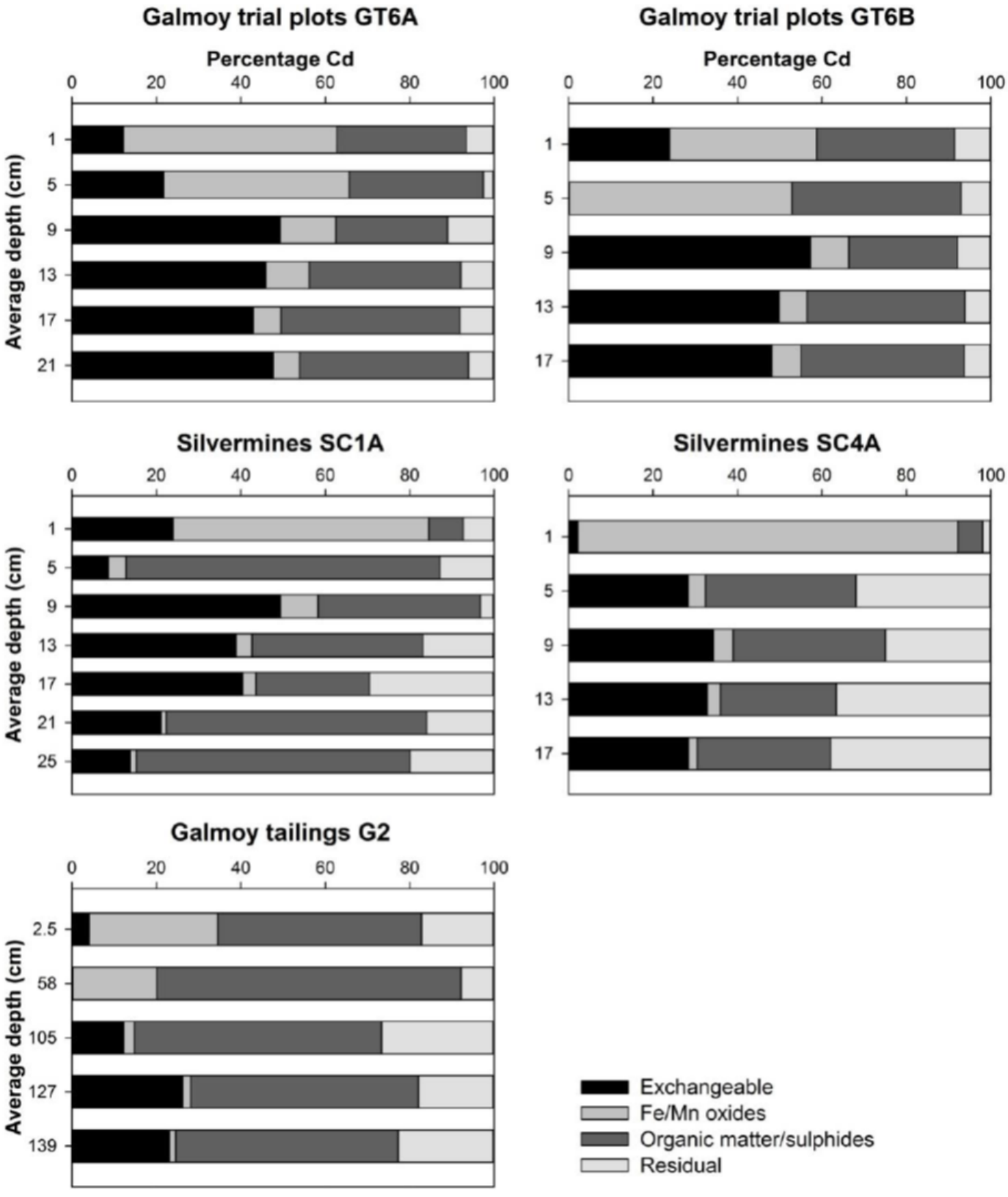
739


STMF1
STMF2
STMF3
STMF4
STMF5
As/Pb (mg kg-1)
Cd (mg kg-1)
Average depth (cm)
Cd
As
Pb

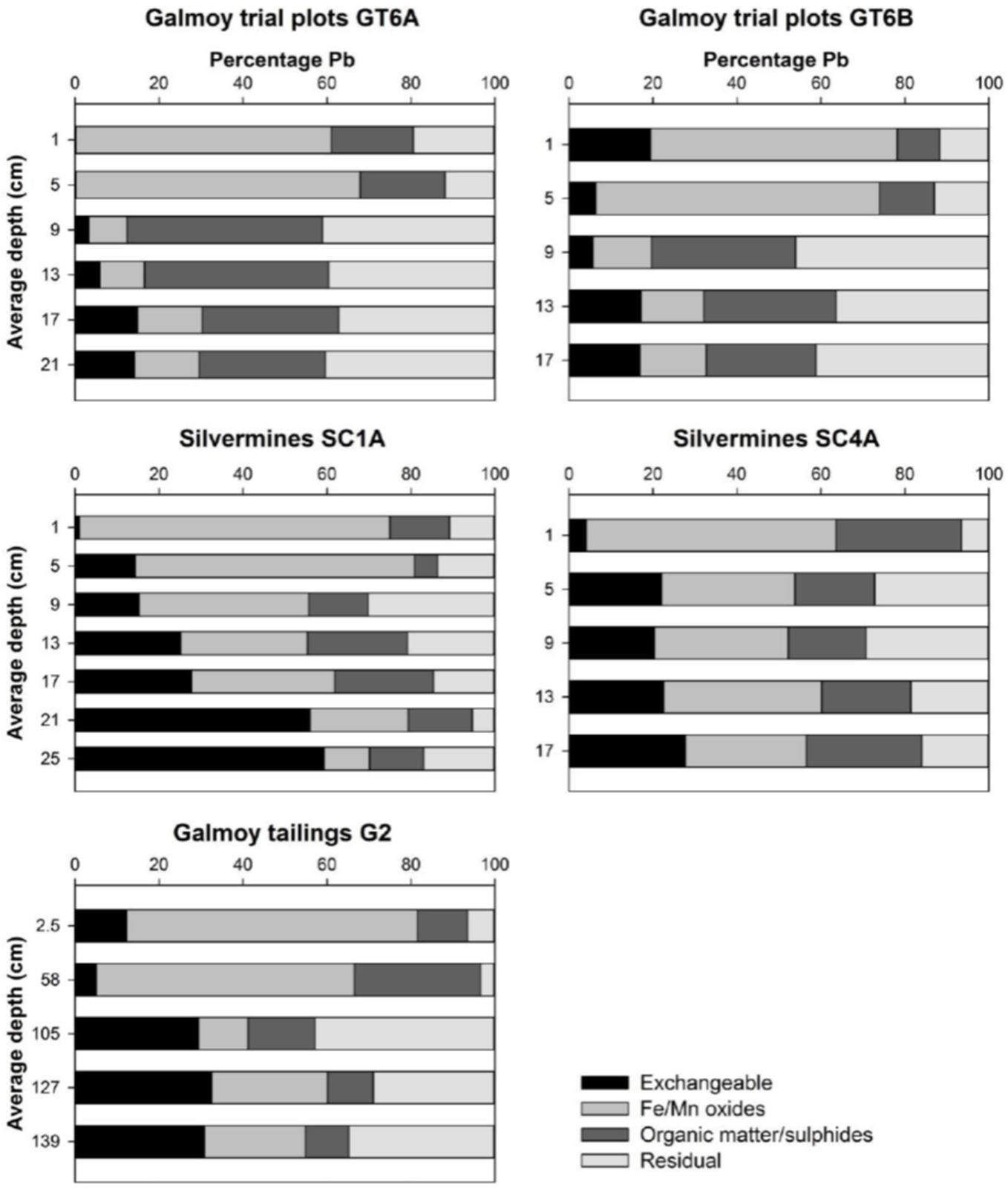
740


Galmoy trial plots GT6A
Percentage As
0
20
40
60
80
100
Average depth (cm)
1
5
9
13
17
21
Galmoy trial plots GT6B
Percentage As
0
20
40
60
80
100
1
5
9
13
17
Silvermines SC1A
0
20
40
60
80
100
Average depth (cm)
1
5
9
13
17
21
25
Silvermines SC4A
0
20
40
60
80
100
1
5
9
13
17
Galmoy tailings G2
0
20
40
60
80
100
Average depth (cm)
2.5
58
105
127
139
Exchangeable
Fe/Mn oxides
Organic matter/sulphides
Residual

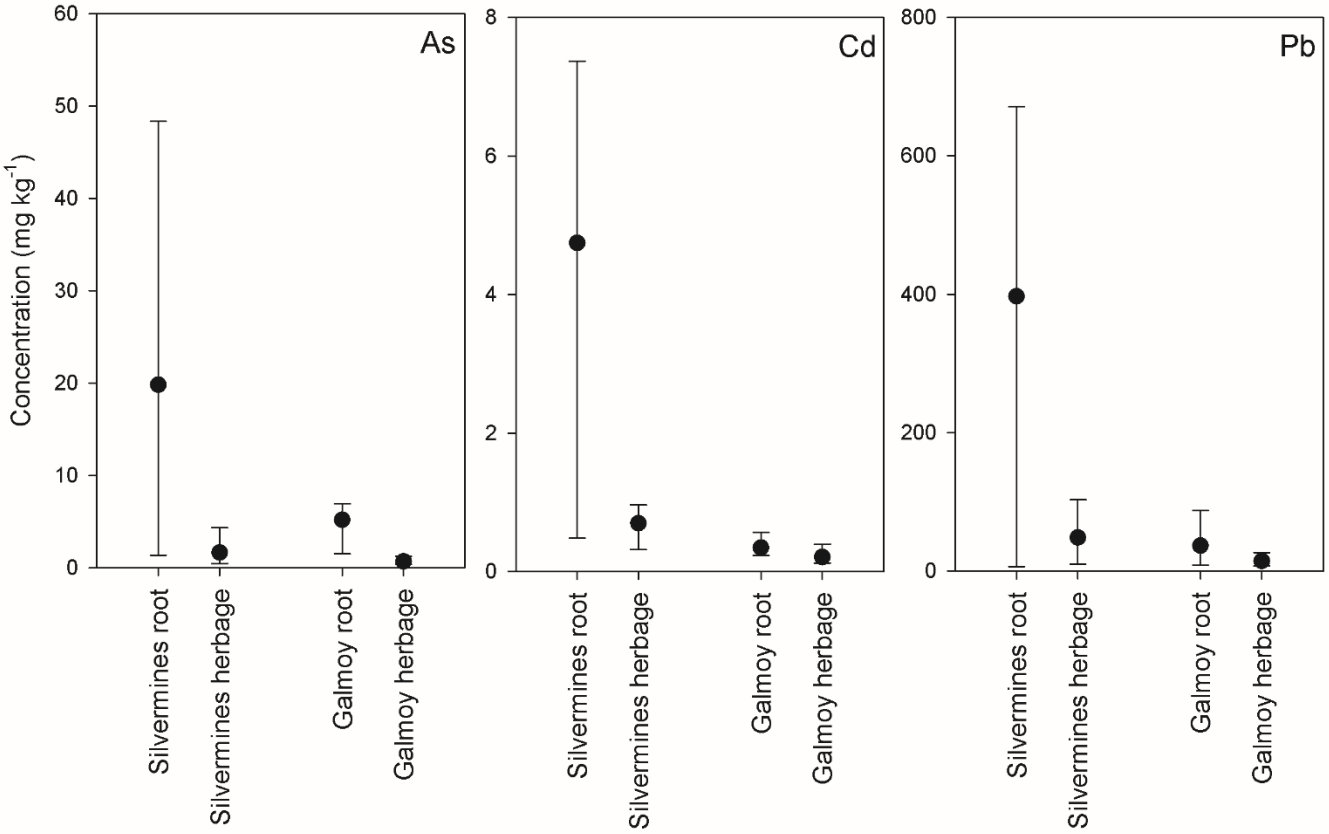
741


Galmoy trial plots GT6A
Percentage Cd
0
20
40
60
80
100
Average depth (cm)
1
5
9
13
17
21
Galmoy trial plots GT6B
Percentage Cd
0
20
40
60
80
100
1
5
9
13
17
Silvermines SC1A
0
20
40
60
80
100
Average depth (cm)
1
5
9
13
17
21
25
Silvermines SC4A
0
20
40
60
80
100
1
5
9
13
17
Galmoy tailings G2
0
20
40
60
80
100
Average depth (cm)
2.5
58
105
127
139
Exchangeable
Fe/Mn oxides
Organic matter/sulphides
Residual

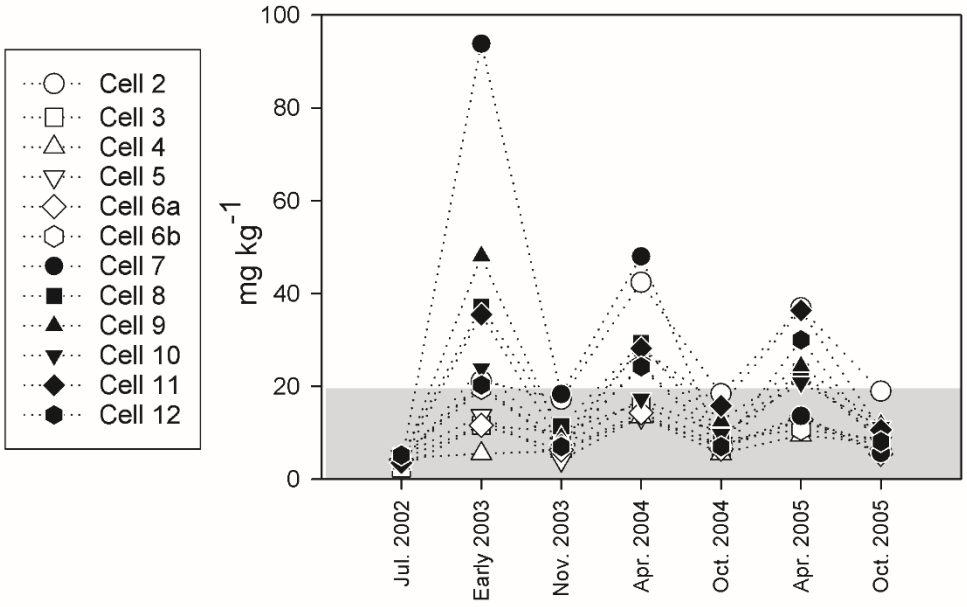
742


Galmoy trial plots GT6A
Percentage Pb
0
20
40
60
80
100
Average depth (cm)
1
5
9
13
17
21
Galmoy trial plots GT6B
Percentage Pb
0
20
40
60
80
100
1
5
9
13
17
Silvermines SC1A
0
20
40
60
80
100
Average depth (cm)
1
5
9
13
17
21
25
Silvermines SC4A
0
20
40
60
80
100
1
5
9
13
17
Galmoy tailings G2
0
20
40
60
80
100
Average depth (cm)
2.5
58
105
127
139
Exchangeable
Fe/Mn oxides
Organic matter/sulphides
Residual

743



744
745
746



747